

Compatibility of Derivatives of 9,10-Dihydroxystearic Acid and 9,10-Dihydroxyoctadecanol With Some Commercial Polymers¹

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DURING the course of our program on the epoxidation and hydroxylation of unsaturated compounds derivable from fats (2, 4, 5, 7) we had occasion also to prepare a large number of esters, ether-esters, and hydroxy-ethers of 9,10-dihydroxystearic acid and 9,10-dihydroxyoctadecanol (3, 6, 8, 9). Since these compounds had low vapor pressures, were insoluble in water, and had a relatively high oxygen content, their possible utilization as plasticizers was considered. This paper briefly describes the results of compatibility tests conducted intermittently during the past five years on many of these compounds with some commercial resins. In one case semiquantitative data are also reported.

The compounds studied were the alkyl (8) and alkenyl (9) esters of low-melting 9,10-dihydroxystearic acid, several 9,10(10,9)-alkoxyhydroxyoctadecanols (6), several esters of 9,10(10,9)-alkoxyhydroxystearic acids (6), and two series of previously unreported compounds, namely, esters of the isomeric 9,10-dihydroxystearic acids with ether-alcohols and polymeric plasticizers prepared by the reaction of selected members of this group of new esters with phthalic anhydride. Commercial polymers employed were ethyl cellulose, cellulose acetate, polyvinyl chloride-acetate copolymers (95:5 and 87:13), polyvinyl butyral (low and high viscosity), and in a few cases, polyvinyl acetate, polystyrene, and a vinylidene chloride-acrylonitrile copolymer.

Experimental

Materials Tested. The preparation of the alkyl (8) and alkenyl (9) esters of low-melting 9,10-dihydroxystearic acid, the 9,10(10,9)-alkoxyhydroxyoctadecanols (6), and the esters of the 9,10(10,9)-alkoxyhydroxystearic acids (6) has already been reported.

A typical preparation of an ester of 9,10-dihydroxystearic acid with an ether-alcohol is described. A mixture of 15.8 g. (0.05 mole) of 9,10-dihydroxystearic acid, m.p. 95°, 7.6 g. of ethylene glycol monomethyl ether (0.10 mole), 0.79 g. of naphthalene-2-sulfonic acid, and 200 ml. of toluene was refluxed for eight hours. The water formed during the reaction was removed azeotropically with the toluene, and the toluene was automatically returned to the reaction mixture. The reaction mixture was evaporated to dryness and the residue was washed three times with hot water. The washed, dried residue, consisting essentially of 2-methoxyethyl 9,10-dihydroxystearate, was obtained in quantitative yield and melted at about 45°. Recrystallization from acetone yielded substantially pure product, m.p. 52.3-53.0°, and saponification number, 153 (calcd. 150). Table I lists the esters prepared by the method just described as well as some of their characteristics. All the recrystallized

products were white solids whereas some of the crude reaction products were liquids.

Ethylene glycol monomethyl ether, b.p. 123-4°, ethylene glycol monoethyl ether, b.p. 134°, ethylene glycol monobutyl ether, b.p. 170°, ethylene glycol mono(2-ethylbutyl) ether, b.p. 197°, ethylene glycol monophenyl ether, b.p. 170° at 100 mm., ethylene glycol monobenzyl ether, b.p. 180° at 98.5 mm., and diethylene glycol monobutyl ether, b.p. 138° at 50 mm., were obtained by multiple fractional distillation of the purest commercial grades through efficient columns (helix packed or heligrid). Diethylene glycol monomethyl ether, b.p. 192° and diethylene glycol monoethyl ether, b.p. 200-1°, were obtained from the purest commercial grades by washing a benzene solution of the ether-alcohol (250 g. per 750 ml. of solvent) with small quantities of water (ca. 5 ml.) to remove water-soluble materials (10 washes), and fractionally distilling the dried benzene solution.

The polymeric plasticizers were prepared by the reaction of equimolar quantities of methyl 9,10-dihydroxystearate, m.p. 70°, 2-butoxyethyl-9,10-dihydroxystearate, m.p. 50°, 2-benzyloxyethyl-9,10-dihydroxystearate, m.p. 45°, and 2-(2-methoxyethoxy)-ethyl-9,10-dihydroxystearate, m.p. 41°, respectively, with phthalic anhydride for one hour at 215-220° and then at 235-240° until the reaction product showed signs of threading. The polymeric plasticizers were pale-yellow to amber colored liquids, insoluble in water.

The stock solutions of commercial polymers had the compositions tabulated below:

Ethyl Cellulose Stock Solution

Ethyl cellulose.....	16 g.
Xylene: butanol (80:20 by volume).....	200 ml.

Cellulose Acetate Stock Solution

Cellulose acetate.....	25-35 g.
Nitropropane.....	90 ml.
n-Butanol.....	37.5 ml.
Ethanol (95%).....	76.5 ml.
Toluene.....	140 ml.

Polyvinyl Chloride: Acetate Copolymer (95:5) Stock Solution

Copolymer.....	16 g.
Butyl acetate: tetrahydropyran (80:20 by volume)	250 ml.

Polyvinyl Chloride: Acetate Copolymer (87:13) Stock Solution

Copolymer.....	16-20 g.
Dioxane or ethylene dichloride: ethanol (90:10 by volume).....	200 ml.

Polyvinyl Butyral Stock Solution

Polyvinyl butyral (high or low viscosity).....	16 g.
Toluene: ethanol (80:20 by volume).....	200 ml.

Polyvinyl Acetate Stock Solution

Polyvinyl acetate.....	16 g.
Xylene: n-butanol (80:20 by volume).....	200 ml.

Polystyrene Stock Solution

Polystyrene.....	16 g.
Xylene: n-butanol (80:20 by volume).....	200 ml.

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Number	R	Crude Esters		Recrystallized Esters		
		Sapon. No. Found	M. P. °C.	Sapon. No.		M. P. °C.
				Calcd.	Found	
1.....	-CH ₂ -CH ₂ -OCH ₃ ¹	164	45-7	150	153	52.3-53.0
2.....	-CH ₂ -CH ₂ -OCH ₃ ²	160	80-5	150	152	89
3.....	-CH ₂ -CH ₂ -OC ₂ H ₅ ¹	144	153	48
4.....	-CH ₂ -CH ₂ -OC ₂ H ₅ ²	144	149	86
5.....	-CH ₂ -CH ₂ -OC ₄ H ₉ ¹	135	136	50
6.....	-CH ₂ -CH ₂ -OC ₄ H ₉ ²	135	138	82
7.....	-CH ₂ -CH ₂ -OC ₆ H ₅ ¹	129	130	78
8.....	-CH ₂ -CH ₂ -OC ₆ H ₅ ²	129	129	100
9.....	-CH ₂ -CH ₂ -OCH ₂ C ₆ H ₅ ¹	125	140	45
10.....	-CH ₂ -CH ₂ -OCH ₂ C ₆ H ₅ ²	125	135	80
11.....	-CH ₂ -CH ₂ -OC ₄ H ₉ (C ₆ H ₅) ¹	126	134	30
12.....	-CH ₂ -CH ₂ -OC ₄ H ₉ (C ₆ H ₅) ²	126	131	80
13.....	-(CH ₂ -CH ₂ -O) ₂ -CH ₃ ¹	134	139	41
14.....	-(CH ₂ -CH ₂ -O) ₂ -CH ₃ ²	134	138	82
15.....	-(CH ₂ -CH ₂ -O) ₂ -C ₆ H ₅ ¹	130	135	38
16.....	-(CH ₂ -CH ₂ -O) ₂ -C ₆ H ₅ ²	130	135	80
17.....	-(CH ₂ -CH ₂ -O) ₂ -C ₄ H ₉ ¹	122	137	41
18.....	-(CH ₂ -CH ₂ -O) ₂ -C ₄ H ₉ ²	122	132	79

¹ Prepared from low-melting 9,10-dihydroxystearic acid, m.p. 95°, and the ether-alcohols.

² Prepared from high-melting 9,10-dihydroxystearic acid, m.p. 130°, and the ether-alcohols.

Vinylidene Chloride-Acrylonitrile Copolymer Stock Solution

Copolymer..... 16 g.
Methyl ethyl ketone..... 400 ml.

In each case the material, the compatibility of which was being tested, was dissolved in about 20 ml. of polymer stock solution, and the resulting solution was spread on a glass plate (6" x 8" x 1/4") by means of a doctor blade. The thickness of the wet film was adjusted to give a dry film about 0.003-0.004" thick. The solvent was allowed to evaporate slowly (several days) in specially constructed boxes which held the plates perfectly flat. The film was removed from the plate, usually by lifting one corner with a razor blade and then soaking the film and plate for a short time in cold water until the entire film was detached. The films were then allowed to hang in the air at room temperature for several days to ensure complete removal of solvent and water. The films were then examined for compatibility of plasticizers. Incompatibility was detected either by hazing of the film, exudation of liquid, or actual crystallization of the material being tested. Control films containing no plasticizer were prepared in all cases. The compatibility tests are summarized in Table II.

The most promising materials were methyl 9,10-(10,9)-methoxyhydroxystearate, compounds 5, 6, 9, and 10 of Table I, and the four polymeric plasticizers listed near the end of Table II. In addition to determining the compatibility of methyl 9,10-(10,9)-methoxyhydroxystearate it was milled with polyvinyl chloride-acetate copolymer (95:5) by a standard technique using the recipe below:

Copolymer..... 63.5 g.
Basic lead carbonate..... 1.0
Stearic acid..... 0.5
Plasticizer..... 35.0

The test data were as follows:

Plasticizer	Milling characteristics	Molded appearance	Compatibility	Elongation, %	Modulus at 100% elongation, psi	Tensile strength, psi
Methyl 9,10-(10,9)-methoxyhydroxystearate	Milled very well, fumed slightly	White, opaque sheet	Borderline; slight exudation at 23°C.	280	1490	2690
Di-(2-ethylhexyl) phthalate	Milled very well, fumed moderately	White, opaque sheet	O.K.	270	1710	3140

These characteristics compare favorably with a control stock plasticized with di-(2-ethylhexyl)phthalate, a well-known commercial plasticizer. Methyl 9,10-(10,9)-methoxyhydroxystearate was also milled with cellulose acetate and was found to be superior to butyl stearate, the control plasticizer, at a concentration of 15%. The flow temperature (1) with the former compound was <103°C., whereas with butyl stearate it was 112°C. Furthermore milling temperatures were about 40°C. lower with methyl 9,10-(10,9)-methoxyhydroxystearate than with butyl stearate. The polymeric plasticizers were not studied further because of the inability to remove phthalic anhydride completely even though the products were washed and heated under vacuum above the sublimation temperature of phthalic anhydride. These materials are of interest however because they are compatible with polymers of such widely different structure.

No attempt has been made to study mixtures of commercial plasticizers with any of the compounds reported in this paper because of the large number of possible combinations. Such a study may prove especially fruitful in the case of borderline plasticizers.

Summary

A study of compatibility with some commercial polymers is reported for some alkyl and alkenyl esters of low-melting 9,10-dihydroxystearic acid, 9,10-(10,9)-alkoxyhydroxyoctadecanols, esters of 9,10-(10,9)-alkoxyhydroxystearic acids, and two series of previously unreported compounds, namely, esters of the isomeric 9,10-dihydroxystearic acids with ether-alcohols and polymeric plasticizers prepared by the reaction of selected members of this group of new esters with phthalic anhydride.

The most promising materials are methyl 9,10-(10,9)-methoxyhydroxystearate, esters of 9,10-dihydroxystearic acid with ether-alcohols, and polymeric plasticizers prepared by the reaction of selected members of this group of new esters with phthalic anhydride.

TABLE II
Compatibility With Commercial Polymers¹

Material Tested	% by Weight of Dry Film	Compatible	Incompatible	Borderline
Methyl 9,10-dihydroxystearate (L.M.) ²	5	1	2	
Methyl 9,10-dihydroxystearate (L.M.).....	15			1
Methyl 9,10-dihydroxystearate (L.M.).....	20		1, 3, 4, 5, 6, 9	
Butyl 9,10-dihydroxystearate (L.M.).....	15	1		
Butyl 9,10-dihydroxystearate (L.M.).....	20		1, 3, 4, 5, 6, 9	
Octyl 9,10-dihydroxystearate (L.M.).....	5			1
Octadecyl 9,10-dihydroxystearate (L.M.).....	5	1	2	
Octadecyl 9,10-dihydroxystearate (L.M.).....	15		1	
Allyl ³ 9,10-dihydroxystearate (L.M.).....	15	1, 2		
Allyl ³ 9,10-dihydroxystearate (L.M.).....	15	5, 6		1
Allyl ³ 9,10-dihydroxystearate (L.M.).....	20		1, 2, 3, 4, 9	5, 6
Methallyl ³ 9,10-dihydroxystearate (L.M.).....	5			2
Methallyl ³ 9,10-dihydroxystearate (L.M.).....	15	1		
Methallyl ³ 9,10-dihydroxystearate (L.M.).....	20		1, 3, 4, 5, 6, 9	
2-Chloroallyl ³ 9,10-dihydroxystearate (L.M.).....	5			2
2-Chloroallyl ³ 9,10-dihydroxystearate (L.M.).....	15	1		
2-Chloroallyl ³ 9,10-dihydroxystearate (L.M.).....	20	5, 6	1, 3, 4, 9	
Oleyl ³ 9,10-dihydroxystearate (L.M.).....	5	1	2	
Oleyl ³ 9,10-dihydroxystearate (L.M.).....	15			1
Furfuryl ³ 9,10-dihydroxystearate (L.M.).....	5	2		
Furfuryl ³ 9,10-dihydroxystearate (L.M.).....	15	1		5, 6
Furfuryl ³ 9,10-dihydroxystearate (L.M.).....	20		2, 3, 4, 5, 6, 9	
9,10(10,9)-Methoxyhydroxyoctadecanol.....	5	2		
9,10(10,9)-Methoxyhydroxyoctadecanol.....	10, 20			2
9,10(10,9)-Ethoxyhydroxyoctadecanol.....	8	2		
9,10(10,9)-Ethoxyhydroxyoctadecanol.....	20		2	
9,10(10,9)-Propoxyhydroxyoctadecanol.....	5	2		
9,10(10,9)-Propoxyhydroxyoctadecanol.....	10			2
9,10(10,9)-Butoxyhydroxyoctadecanol.....	5	2		
9,10(10,9)-Butoxyhydroxyoctadecanol.....	10			2
9,10(10,9)-Alloxyhydroxyoctadecanol ⁴	5	2		
9,10(10,9)-Alloxyhydroxyoctadecanol ⁴	20			
Methyl 9,10(10,9)-Methoxyhydroxystearate.....	15	1		2
Methyl 9,10(10,9)-Methoxyhydroxystearate.....	35	4		3
Ethyl 9,10(10,9)-Ethoxyhydroxystearate.....	5	2, 4		
Ethyl 9,10(10,9)-Ethoxyhydroxystearate.....	10			2, 4
Allyl 9,10(10,9)-Alloxyhydroxystearate ⁵	5	1, 2		
Allyl 9,10(10,9)-Alloxyhydroxystearate ⁵	20		2	
Compounds 1 and 2, Table I.....	20		2	1
Compounds 3 and 4, Table I.....	20		2	1
Compounds 5 and 6, Table I.....	20	1, 3, 5, 6	2, 4, 7, 8, 9	
Compounds 7 and 8, Table I.....	20		1, 2	
Compounds 9 and 10, Table I.....	20	1, 3, 5, 6	2, 4, 7, 8, 9	
Compounds 9 and 10, Table I.....	30		3	5, 6
Compounds 11 and 12, Table I.....	20		2	1
Compounds 13 and 14, Table I.....	20		2	1
Compounds 15 and 16, Table I.....	20		2	1
Compounds 17 and 18, Table I.....	20		2	1
Polymeric Plasticizer A ⁶	20	1	2	
Polymeric Plasticizer A ⁶	30	3, 5, 6		
Polymeric Plasticizer B ⁶	20	1	2	
Polymeric Plasticizer B ⁶	30	3, 5, 6		
Polymeric Plasticizer C ⁶	20	1	2	
Polymeric Plasticizer C ⁶	30	3, 5, 6		
Polymeric Plasticizer D ⁶	20	1	2, 8, 9	
Polymeric Plasticizer D ⁶	30	3, 5, 6		

¹ Commercial polymers are listed in the compatibility columns under the following code: 1 = ethyl cellulose; 2 = cellulose acetate; 3 = polyvinyl chloride-acetate copolymer (95:4); 4 = polyvinyl chloride-acetate copolymer (87:13); 5 = polyvinylbutyral, low viscosity; 6 = polyvinylbutyral, high viscosity; 7 = polyvinyl acetate; 8 = polystyrene; 9 = vinylidene chloride-acrylonitrile copolymer.

² L.M. means prepared from low melting 9,10-dihydroxystearic acid, m.p. 95°.
³ Films darkened on exposure to air.
⁴ Prepared from phthalic anhydride and methyl 9,10-dihydroxystearate, m.p. 70°.
⁵ Prepared from phthalic anhydride and compound 9 of Table I.
⁶ Prepared from phthalic anhydride and compound 5 of Table I.
⁷ Prepared from phthalic anhydride and compound 13 of Table I.

droxystearic acid with ethylene glycol monobutyl ether and ethylene glycol monobenzyl ether, and the polymeric plasticizers. The last-named group is compatible with polymers which differ widely in chemical structure.

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